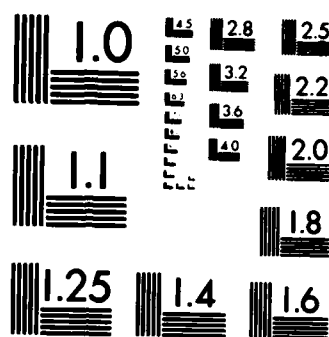


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OBSERVATION OF A NOVEL LOW-LYING EXCITED STATE IN ZINC(II) COMPLEXES

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Abstract

A novel low-lying excited state(s) has been observed from emission studies of complexes of the type $M(\text{BS})_2(\text{s-phen})$ [$M = \text{Zn(II)}, \text{Cd(II)}$; BS = benzene thiol; s-phen = substituted 1,10-phenanthroline] at 77 K. The state is tentatively assigned to a charge-transfer configuration in which the thiol donates charge through the closed d-shell to the N-heterocyclic acceptor. The emission is broad, indicating substantial distortion of the excited state geometry with respect to the ground state. The state decays on the order of microseconds, but its spin signature has not yet been determined.

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IN ZINC(II) COMPLEXES

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Photoluminescence spectra of closed shell zinc(II) complexes containing both N-heterocyclic and aromatic thiol ligands reveal the presence of a previously uncharacterized excited state. Modifications of the complexes by changing the pi-donating strength of the substituents on the thiol moiety produce substances ranging from those in which the presence of the low-lying state is barely detectable to compounds whose emission spectra are dominated by the new transition. The experimental observations on a typical set of analytically pure compounds are reproduced in the figure.

When the $\text{ZnCl}_2(\text{phen})$ complex, a white solid, is illuminated by ca. 330 nm uv light in an organic glass at 77 K, strong fluorescence and phosphorescence characteristic of the phen ligand are observed (1). Replacement of the chlorides by two pentafluorothiophenol anions ($\text{F}_5\text{-PhS}$) produces a slightly off-white solid that exhibits no phen fluorescence but does show a strong phen phosphorescence. Intensive studies of this latter emission reveal the presence of a new band maximizing at ca. 620 nm lying in the tail of the phen phosphorescence. The band shows up clearly in time-resolved spectra. Replacing the chlorides in $\text{ZnCl}_2(\text{phen})$ by the anions of 4-chlorothiophenol (4-Cl-PhS) produces a molecule in which the new band dominates the emission spectrum as is clearly seen in the figure. Phen phosphorescence is not entirely quenched, however. Finally, excitation of the $\text{Zn}(4\text{-MeO-PhS})_2(\text{phen})$ complex [4-MeO-PhS = anion of 4-methoxythiophenol] produces only the broad new band maximizing ca. 620 nm. (The presence of an aromatic thiol is necessary; aliphatic thiols do not produce

compounds exhibiting the new band.) Although the observed structured fluorescence and phosphorescence clearly originate from the phen ligand, the subtle differences both of the spectra themselves and, in the case of the phosphorescence, the measured lifetimes decisively show that the phen ligand is coordinated to the zinc ion.

Detailed spectroscopic measurements, including time-resolved studies, determine that the new band arises from an excited state that (a) is only present when both N-heterocyclic and aromatic thiol ligands are coordinated to the Zn(II) ion, (b) decays on the order of microseconds at 77 K, (c) is tunable to some extent by making judicious changes in either or both types of ligand, (d) profoundly affects the radiationless degradation rates and pathways in the complexes, and (e) is a general property of these types of complexes of metal ions with filled d-shells. We have in the laboratory analogous results from Cd(II) (2) and Sn(IV) systems (3).

Absorption measurements of these types of complexes show the presence of a broad low-lying transition(s) that gradually shifts toward the visible (see Fig.) as the electron donating ability of the thiol ligand increases. This new band correlates with the presence of the novel emission band and is responsible for the progressive change in color of the complexes from white (ZnCl_2phen) to yellow $[\text{Zn}(4\text{-MeO-PhS})_2(\text{phen})]$ in the crystalline state. The behavior of this absorption band in Zn(II) complexes has been noted previously by Koester (dithiol ligands)(4), who assigned it to an interligand trans-metallic charge-transfer (ITCT) transition between the thiol donor and the N-heterocyclic acceptor. We tentatively assign the new emitting state(s) to an ITCT transition(s), although the new emission band is not the inverse of the absorption band. Both the ITCT orbital designation and the spin multiplicity of the new excited state are still not definitively characterized.

Detailed spectroscopic studies between 77 K and 4 K of these types of zinc(II) molecules and other (nd)¹⁰ (n = 3,4) complexes containing various N-heterocyclic ligands and both mono and dithiol ligands will be published elsewhere.

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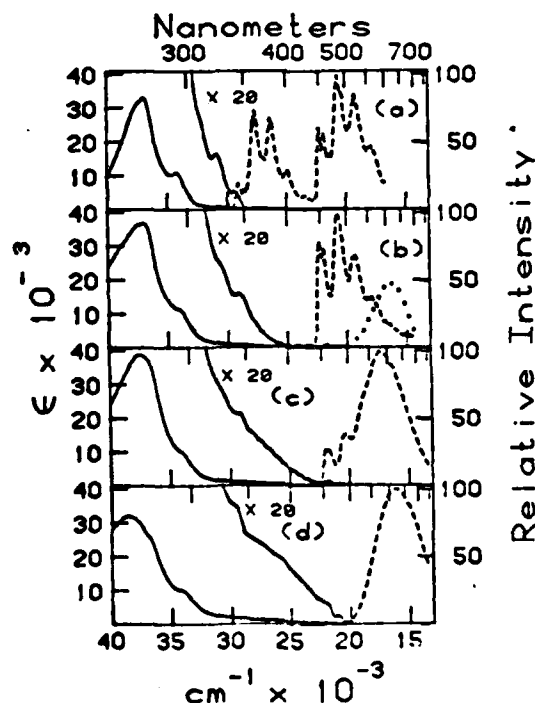


Figure 1. Absorption (—, RT) and corrected emission (---, 77 K) spectra of zinc(II) complexes in $\text{CHCl}_3/\text{EtOH}$; 1:19, v/v. (a) $\text{ZnCl}_2(\text{phen})$, (b) $\text{Zn}(\text{F}_5\text{PhS})_2(\text{phen})$; a time-resolved emission spectrum (· · · ·) at 77 K is included (0.5 μs window; 1 μs delay), (c) $\text{Zn}(4\text{-Cl-PhS})_2(\text{phen})$, (d) $\text{Zn}(4\text{-MeO-PhS})_2(\text{phen})$.

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